FINAL

Department of Water Resources
Equipment Performance Criteria Study
Phase I: Portable Field Instruments

by

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1.1 INTRODUCTION

In accordance with Water Resources Engineering Memorandum No. 60 (WREM 60), which establishes policy and procedure to assure that quality assurance/quality control measures are implemented throughout the Department of Water Resources (DWR), Phase I of an Equipment Performance Criteria study was conducted. The purpose of Phase I was to evaluate specific types of field and laboratory analytical equipment, to assess the quality of data provided by these instruments, and determine the comparability of these data. The instrument parameters of interest in this study were pH, dissolved oxygen, temperature, turbidity, and specific conductance. The results of the study should be of value to DWR Program Managers and staff who purchase and use instruments which measure for these parameters.

1.2 SURVEY OF INSTRUMENTS

To evaluate instruments purchased and utilized by DWR employees, tests were made on DWR field and laboratory instruments. Surveys were sent out in 1995 that queried DWR personnel as to the availability of their specific instruments for testing, and a possible time frame available for site visits and testing. The results of these surveys were used to plan site visits. Many units and divisions participated in these surveys and facilitated completion of the equipment performance study. The participants are listed below in Table 1.

From those units that sent in surveys and participated in this study an equipment inventory which lists all instruments tested was developed. The complete inventory list is located in Appendix A. Table 2 below provides a summary list of types and manufacturers of instruments DWR currently uses for field measurements. This table also indicates contact numbers for service and sales from the major manufacturers surveyed in this study and whether or not the equipment is currently supported by the manufacturer.

Table 1
Equipment Performance Study Participants

Division	District	Field Unit	DWR Contact
Local Assistance	Headquarters	Field Unit	Steve Belluomini
Local Assistance	Headquarters	Bryte Lab	Bill Nickels

Division	District	Field Unit	DWR Contact
Local Assistance	Central	Ground Water Unit	Jim Gibboney
Local Assistance	Central	Surface Water Unit	Rich Pendelton
Local Assistance	Northern	Water Quality & Biology Unit	Gerald Boles
Local Assistance	San Joaquin	Surface Water & Data Unit	Holly Ferrin
Local Assistance	Southern		Gary Gilbrath
ESO		Ag Diversion Study	Leo Winternitz
ESO		San Carlos	Scott Waller
O&M	Beckwourth		Ralph Howell
O&M	Oroville	Field Div. Water Operations	John Knox

Table 2
Equipment Manufacturers and Support

Parameter	Manufacturer	Telephone	Model(s)	Number of Instruments Tested	Supported
EC	Yellow Springs Inc	(513) 767-7241	3000TLC, 30, 33	15	Yes
EC	VWR Scientific Instruments	1 (800) 932-5000		1	Yes
EC	Beckman (Rosemont Analytical)	1 (800) 742-2345	RC 20, RC 19	6	RC 20 Yes RC 19 No
EC	Oakton	1 (800) 323-4340	EC100	2	No
EC	Orion	1 (508) 922-4400	124	6	No (however parts are still available)

Parameter	Manufacturer	Telephone	Model(s)	Number of Instruments Tested	Supported
EC	Hach	1 (970) 669-3050	17250	1	No
EC	Myron & Co		532M1	1	No
EC	Hanna Inst.	(+44) 1525-8508 55	HI8733	1	Yes
EC	Radiometer America		CDM 83	1	No
pH	Beckman	1 (800) 742-2345	ϕ21, ϕ10, ϕ63	7	Yes
pH	Orion	1 (508) 922-4400	610, 250A, 230A, 265	6	Yes
pH	Hellige (from VWR)	1 (800) 932-5000	Color Comparator	10	Yes
pH	Hach	1 (970) 669-3050	43800	2	Yes
DO	Yellow Springs Inc	(513) 767-7241	50, 50B	7	50B Yes 50 No
DO	Winkler (parts from VWR)	1 (800) 932-5000	N/A	11	N/A
DO	Hach	1 (970) 669-3050	Portable	1	Yes
DO	Orion	1 (508) 922-4400	820	1	Yes
Turbidity	Hach	1 (970) 669-3050	2100P, 2100A,	9	2100P Yes 2100A No
Turbidity	Turner	1 (408) 749-0994	Turner Design	1	No
Temperature	Yellow	(513)	2100, 57,	6	2100 Yes

Parameter	Manufacturer	Telephone	Model(s)	Number of Instruments Tested	Supported
	Springs	767-7241	44TD, 50B, 33		57 Yes 50B Yes 33 Yes 44TD No
Temperature	VWR Scientific	1 (800) 932-5000	Digital Therm. Glass Therm	2	Yes
Temperature	Fluke	1 (206) 356-5783	51	4	Yes
Temperature	Ertco-Glass (from VWR)	1 (800) 932-5000	ASTM 36C	1	No
Multi	Hydrolab	1 (800) 949-3766	Data Sound 3-3	1	No

1.3 GENERATION OF EQUIPMENT PERFORMANCE DATA

The methods employed by QA/QC staff in obtaining data for the study were consistent for sampling methods, calibration procedures, test/retest, and records of observations. The goal in evaluating the data obtained was to be able to estimate the average precision of each type of instrument and what variability one could expect when using different instruments. In other words, what variability one might expect when taking replicate readings of a water parameter, and what one would see if the readings were taken using separate instruments. These variability values differ for each parameter (i.e. pH, turbidity, or temp) and between differing DWR instruments.

To find the answers we determined which instruments were in good working order and ready for testing. We then numbered each instrument and recorded the number on an inventory list. In this study we tested over 100 instruments department- wide to obtain an overall picture of the state of DWR testing equipment. We tested each instrument with three standards covering low, mid, and high ranges for each field parameter.

For pH and turbidity we purchased standards from Environmental Resource Associates (ERA). For temperature and specific conductance, we purchased and utilized NIST certified reference instruments. For dissolved oxygen the Winkler titration method was used to provide reference values for the samples tested. In Appendix B one can find a detailed description of the statistical methods utilized in this study to process the measurement data obtained.

From the data obtained in testing DWR field instruments, two critical values were calculated. These values are both measures of the variability one generally sees in using instruments to obtain field parameter values. Formally, this variability can be described using two terms: repeatability and reproducibility. Repeatability is the closeness of agreement between successive results obtained with the same method on identical test material and under the same conditions (same operator, same instrument and same time). Reproducibility is the closeness of agreement between individual test results obtained with the same method on identical test material but under different conditions (different operator, different instrument, and/or different time) (Steiner, 69).

For our purposes, repeatability is the measure of precision between instrument readings, and reproducibility is a measure of precision between the same instrument parameter at differing sites. It was from these two measures of variability that conclusions were made in order to assess the precision of test instruments utilized by DWR personnel in field and laboratory sampling procedures. The measures of variability obtained could conceivably become department-wide standards for the parameters that have been tested in this study. The goal of obtaining measurements of repeatability and reproducibility is to give Program Managers reliable information on which to base decisions of equipment use and future procurement.

1.4 EQUIPMENT TESTING PROTOCOL

An equipment testing protocol, outlined below, was developed for use during site visits.

I. Prior to site visit

- Make telephone contact with site: identify contact person, schedule site visit, inform site staff individual of order in which equipment will be run, and request that instruments be in “field ready” condition upon arrival of DLA staff. Inform site contact person that we will make parameter measurements. (Remind site contact person that time can be billed to this project).

- Prepare kit of reference standards and/or traceable reference instruments and self-prepared proximate standards, plus glassware and supplies for site visit (refer to appropriate checklist).

- For each site determine order in which equipment parameters will be run.

- Prepare data entry, equipment description/identification, and field questionnaire sheets for site visit.

II. During site visit

- Have local personnel or study team calibrate instruments using standard procedures.

- Provide feedback at end of measurement cycle for each parameter measured. If unsatisfactory results have been obtained, inform site staff person and work with them to re-calibrate, etc. and re-measure the parameter.

- While making parameter measurements refer to instrument manuals, SOP's, and/or the DWR Sampling Manual (Chapter 7 - Field Analyses) or the DWR MWQI Program Field Manual (Chapter 2 - Water Quality Field Measurements) for guidance, if needed.

- When parameter measurements are re-taken, make proper notes to assure that the proper values will be reported in database.

- Following parameter measurements, clean up and repack instruments and supplies for return to base.

III. Post site visit

- At conclusion of site visit, make notes on areas where DLA could provide assistance and/or training for unit personnel.

- Follow up site visit with a "thank you" telephone call to contact person(s).

1.5 RESULTS

Overall in this study measurements of pH were made on 20 different instruments (10 were color comparators). For specific conductance a total of 31 meters were tested, 10 meters were tested for turbidity, 42 meters for temperature, and 6 for dissolved oxygen (DO). In addition, 10 Winkler units were tested for DO. The measurement data obtained from the instruments tested is listed by parameter in Appendix C.

To draw useful conclusions from the data, values of repeatability and reproducibility were statistically calculated. As stated earlier in this report, repeatability is the measure of precision between replicate readings made on the same instrument and reproducibility is the measure of precision between instruments. One would expect the value for reproducibility to be greater than the value calculated for repeatability. That is, one expects to obtain more consistent readings on the same instrument than when one changes from a particular instrument to another. If the values for repeatability were found to be greater than those for reproducibility, questions would arise surrounding the precision of sampling techniques performed in the field or laboratory.

The repeatability and reproducibility measures of variability for the five test parameters are shown below in Table 3. It was noted that for measurements of pH, temperature, and dissolved oxygen, that the instrument values had essentially the same amount of variability at low and high range readings. On the other hand, with measurements of EC and turbidity the variability in instrument readings increased as the parameter value increased. For these latter two parameters, the relative amount of variability stayed constant over the range of parameter values. To better illustrate situations where the variability is relative to the measured value, the variability coefficients (repeatability and reproducibility) were recalculated to relative percent values and reported in Table 4. The data for all parameters in statistically adjusted form are in Appendix D.

A total of 10 pH meters manufactured by Beckman and Orion were tested. In addition, 10 color comparators manufactured by Hellige were tested. From all of the measurements made a value of ±0.05 pH units was calculated for repeatability, and a value of ±0.13 pH units was calculated for reproducibility.

The standards utilized to cover a range of pH values were prepared to have certified values (Environmental Resource Associates) of 6.4, 7.5, and 8.8 pH units, respectively. These standards were chosen to represent typical environmental values that might be encountered by DWR personnel making field measurements. Of the meters and parameters tested for in this study, DWR pH meters (Beckman and Orion) appear to be the most precise of all DWR instruments tested. Results for repeatability and reproducibility for DWR pH meters (±.05 and ±0.13 pH units, respectively) were found to be well within acceptable limits of variability.

Table 3
Variability in Instrument Readings - Absolute Values

Parameter	Units	Repeatability	Reproducibility	Total Number of Instruments Tested
pH	pH Units	0.05	0.13	20
Temperature	Degrees C	0.17	0.32	42
Dissolved Oxygen	mg/L	0.59	0.66	6
Specific Conductance	μS/cm	68.25	223.06	31

Parameter	Units	Repeatability	Reproducibility	Total Number of Instruments Tested
Turbidity	**NTU**	**0.35**	**2.25**	**10**

Table 4
Variability in Instrument Readings Calculated as the Relative Percent

Parameter	Units	Repeatability	Reproducibility	Total Number of Instruments Tested
pH	**pH Units**	**0.70%**	**1.31%**	**20**
Temperature	**Degrees C**	**2.32%**	**6.96%**	**42**
Dissolved Oxygen	**mg/L**	**6.25%**	**7.15%**	**6**
Specific Conductance	**μS/cm**	**0.82%**	**2.89%**	**31**
Turbidity	**NTU**	**2.81%**	**8.84%**	**10**

Calculated values for relative percent variability produced a repeatability result ±0.7% of a pH unit, and a reproducibility ±1.31% of a pH unit.

The color comparators tested were shown to be precise to ±0.2 pH units, which is satisfactory for most environmental measurements. Color comparators are subject to a number of qualitative factors which include the need for outdoor lighting when reading the instrument, the possibility of color blindness affecting the results, and the fact that this instrument takes an experienced user to obtain accurate readings.

A total of 31 specific conductance (EC) meters manufactured by Yellow Springs, VWR Scientific, Orion, Beckman, Hach, and Radiometer America were tested. The standards were prepared for EC values of 104, 2506, and 8816 μS/cm for low, mid, and high ranges, respectively. These EC meters exhibited essentially the same relative variability over this range of samples tested. Results for EC were found to have variabilities of ±0.82% (relative μS/cm) for repeatability and ±2.89% for reproducibility. These results for variability indicate that at ~100 μS/cm (low range) the repeatability is approximately ±1μS/cm and the reproducibility is approximately ±3 μS/cm. At ~ 9000 μS/cm (high range), the repeatability variability is approximately ±90 μS/cm and the reproducibility variability is approximately ±270 μS/cm. Over the range of sample ECs tested the less than ±3% variability between instruments is acceptable.

A total of 10 turbidity instruments manufactured by Hach and Turner were tested. The standards purchased for turbidity from ERA had certified values of 1.5, 12, and 35 NTU for low, mid, and high ranges, respectively, as one might expect to find in the environment. Relative percent variabilities for turbidity were found to be ±2.81% (relative NTUs) for repeatability and ±8.84% for reproducibility. Over the range of readings between 1.5 and 35 NTU these results for variability indicate that repeatability at 1.5 NTU (low range) is variable by approximately ±0.04 NTU while reproducibility is variable by approximately ±0.13 NTU. At the 35 NTU value (high range), the repeatability variability is approximately ±1 NTU and the reproducibility variability is approximately ±3 NTU.

Because of the low number of DO meters tested (manufactured by Hach and Yellow Springs) values from only six instruments were included in the variability calculations for DO. As a result, the variability results are subject to some qualification. The standards prepared for DO were 3.09, 8.97, and 11.87 mg/L for low, mid, and high ranges, respectively. These values were verified by Winkler titration. The calculated variability results for dissolved oxygen (DO) were ±0.59 mg/L for repeatability, and ±0.66 mg/L for reproducibility.

A total of 10 DO Winkler titration units were also tested. Separate values for Winkler performance were calculated. In evaluating the Winkler units, split samples were analyzed so that the quality of reagents used in field operations could be compared to reference reagents. Where field units had more than one Winkler setup, the reagents were tested in only one unit. Overall in this study no statistically significant differences were found between the performance of the Winkler units tested and the reference test measurements. Thus the quality of reagents currently being employed to carry out this method is high. An average difference between the readings from the Winkler units tested was calculated to be less than ±0.2 mg/L oxygen. In addition, a t-test was performed by QA/QC staff on data obtained from the Winkler units. The results obtained indicate that at a 95% confidence limit, the actual variance is less than would be statistically expected between instruments. The data, calculations, and results are located in Appendix C in the DO section.

A total of 42 instruments including those manufactured by Yellow Springs, VWR Scientific, Fluke, plus a number of glass thermometers were tested for temperature. The majority of these instruments had another primary function (EC or pH etc.); temperature readings were a secondary function of the instrument. The standards used for low, mid, and high temperatures were 2.6, 20.5, and 29.7 degrees Celsius, respectively. Results for temperature indicate a repeatability variability of ± 0.17 of a degree Celsius and a reproducibility variability of ±0.32 of a degree. In general, all DWR temperature devices were found to be quite precise between various field instruments, as well as, between measurements. To better indicate the variability observed with various instruments, a series of graphs were prepared. Figures 1 through 3 contain charts which visually indicate the absolute variability for pH, temperature, and DO. Relative percent charts for EC and turbidity are also found in Figures 4 and 5.

A number of instruments were identified at the time of our field unit visits as producing data unaccepatable for inclusion in the study. These instruments had problems ranging from difficulty in calibraton to rechargable batteries that were not charged at the time of our field visit. A total of six instruments were not included in the study due to various problems. One pH meter was difficult to read due to a cracked display, but the data obtained were utilized in the study. The instruments not included in the study are shown in Table 5 below.

In addition, turbidity meter #99 was retested (it was originally numbered 26) after the instrument was returned from the manufacturer with its optics upgraded. In comparing the results obtained from turbidity meter 99, before and after it was sent to the factory, no appreciable difference between instruments was determined. The new data from the instrument are found in Appendix C.

Table 5
Instruments not included in Data Tables

Instrument Number	Parameter	Problem
9	pH	Would not calibrate
21	pH	Crack in display, difficult to read (data were utilized in study)
28	Turbidity	Needs factory calibration
99*	Turbidity	Retested after optics upgrade (data were utilized in study)
79	DO	Meter appeared to drift when measuring DO
86	pH	Battery dead

Instrument Number	Parameter	Problem
85	EC	Meter only reads to a level of 2500μS/cm
96	DO	Battery dead

*Originally tested as instrument #26.

1.6 CONCLUSIONS

Environmental parameters of pH, temperature, specific conductance (EC), dissolved oxygen, and turbidity are routinely being measured by DWR personnel using field quality equipment. Based on this study in which over 100 instruments were surveyed, with few exceptions, the quality of measurement values obtained was high. DWR field unit instruments are capable of measuring pH within ±0.2 pH units, temperature within ±0.32 degree Celsius, EC within ±3% of the measured μS/cm value (±3 μS/cm @ 100 μS/cm), dissolved oxygen within ±0.7 mg/L (instrument) or ±0.2 mg/L (Winkler titration), and turbidity within ±9% of the measured NTU value (±1.1 NTU @ 12 NTU). Overall, the reproducibility values for pH, temperature and EC represent excellent performance by field equipment. The reproducibility values for DWR DO meters and turbidimeters are satisfactory for typical field parameter measurements. These values, for the latter two parameters, may well be overstating the potential variability for these measurements, due to the limited number of instruments available for testing.

Figure 1

Chart of Absolute Values for pH

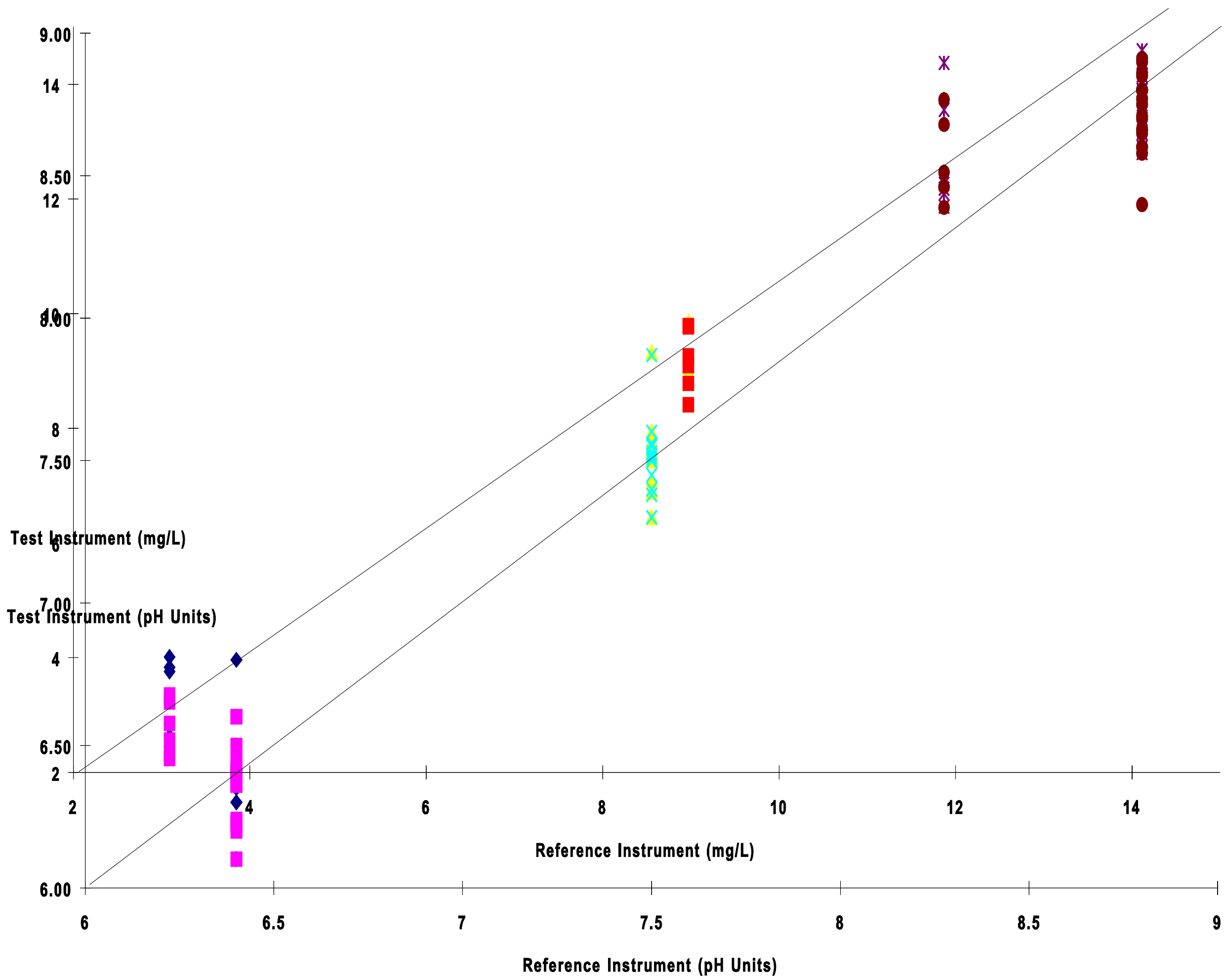

Figure 2
Chart of Absolute Values for DO

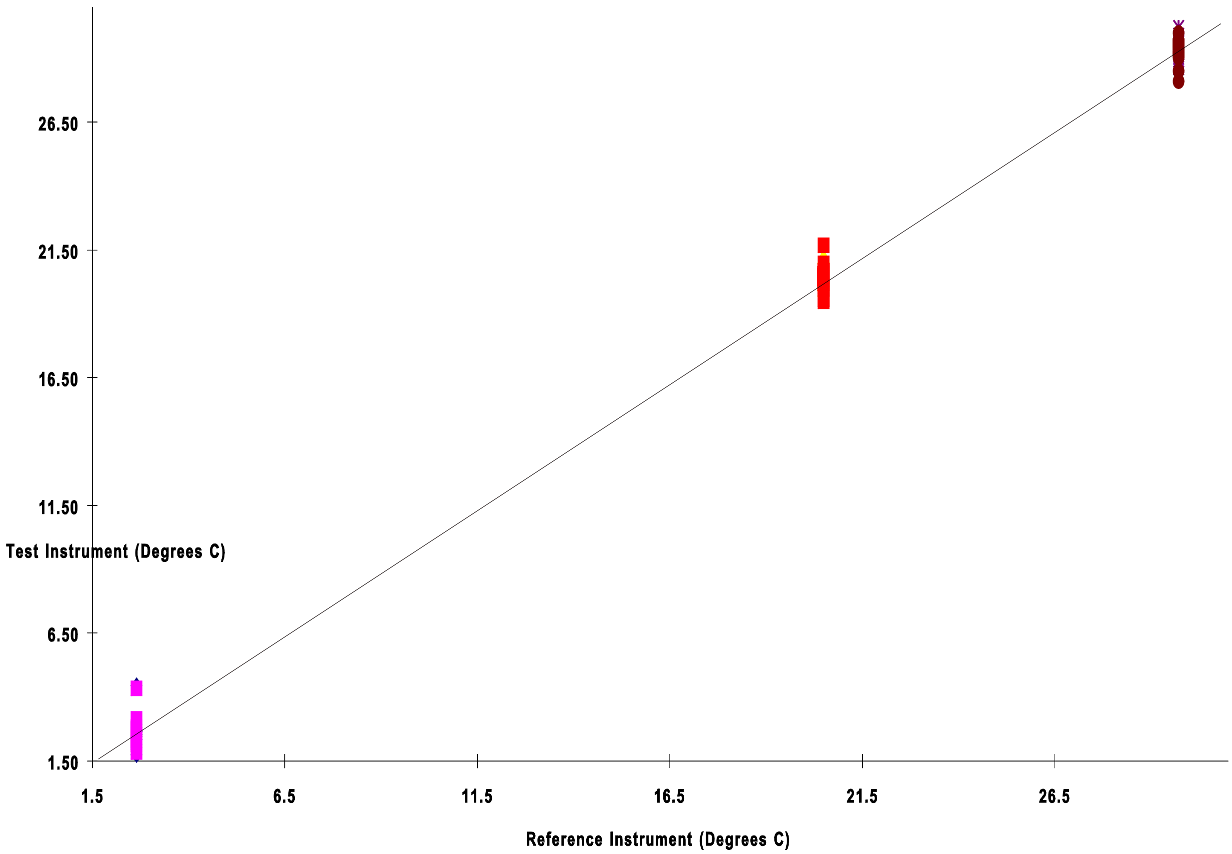

Figure 3
Chart of Absolute Values for Temperature

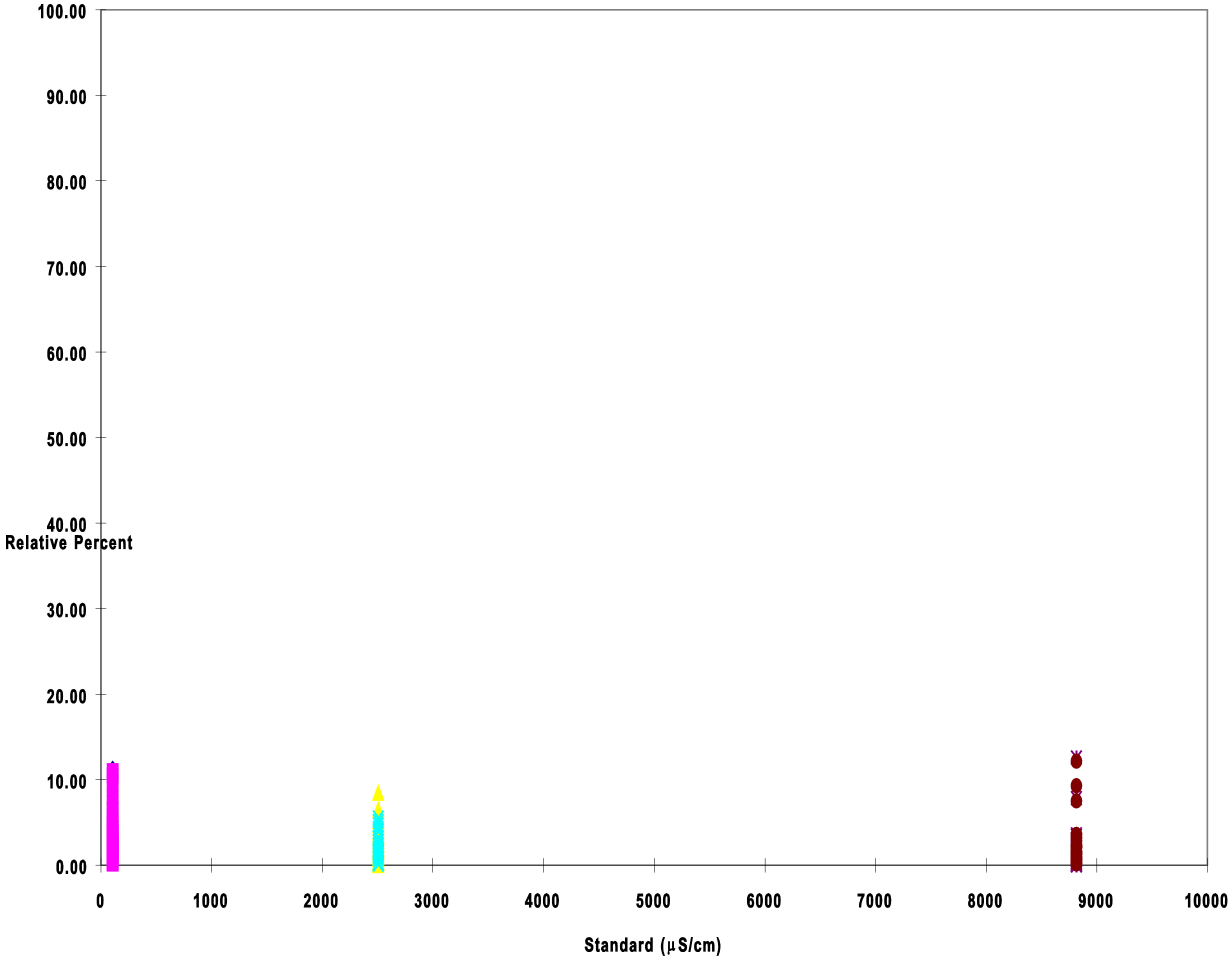

Figure 4
Chart of Relative Percent Values for EC

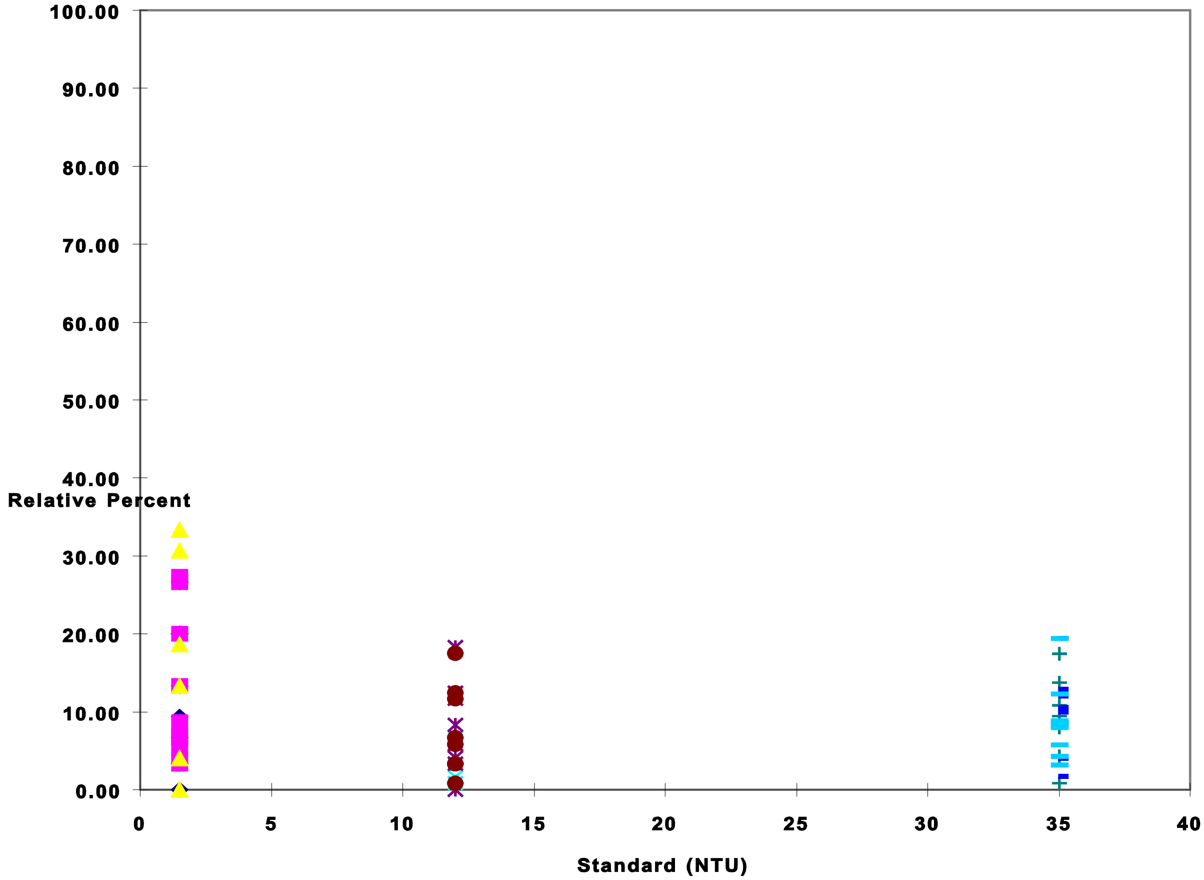

Figure 5
Chart of Relative Percent Values for Turbidity

1.7 FUTURE ACTIVITIES

Phase I of the Equipment Performance Criteria study was purposefully set up to monitor portable field equipment where it would be straightforward to acquire certified reference standards and/or certified reference instruments. As originally envisioned, Phase I would be followed with Phase II and Phase III:

Phase II: Evaluation of stationary and continuous water quality monitoring equipment

Phase III: Development and operation of an ongoing quality control program for water quality monitoring equipment for:

(A) stationary monitoring equipment
(B) portable field monitoring equipment

As stated at the June, 97 QC Committee meeting, continuous monitoring instruments provide 10 - 30 times the amount of data as grab-sample equipment. Furthermore the regular, continuous nature of the former data makes it quite valuable, especially in modeling activities. Up until the present there has not been any QA Unit activity towards evaluating the performance of the Department's stationary monitoring equipment. A program for accomplishing this study is being initiated.

Once a stationary equipment monitoring program is underway it will be possible to design an ongoing evaluation program for all the Department's water quality monitoring equipment. A tenant of quality control is that one must continuously demonstrate that one is "in control" of the measurement process. The scope and frequency of two ongoing evaluation programs for stationary and portable field monitoring equipment can be planned so as to provide a high level of confidence in the Department's data to all users of these data.

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